

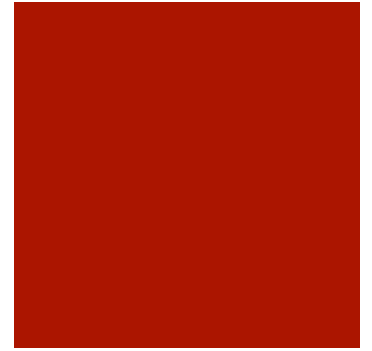
# High Capacity, Low-Voltage Titanate Anodes for Sodium Ion Batteries

Project ID # BAT428

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# Overview



## Timeline

- Project start date 10/1/2018
- Project end date 9/30/2021
- Percent complete 12.5%

## Barriers

- Barriers addressed
  - Cost
  - Concerns about Co

## Budget

- Total Project Funding
  - DOE share 100%
  - Contractor share N/A
- Funding for FY 2019 \$300k

## Partners

- LBNL, Army Research Lab
- Project Lead: LBNL



# Relevance

- Na-ion batteries are a possible drop-in replacement for Li-ion batteries
  - Similarity in concept means we can leverage engineering knowledge (closest “beyond lithium ion” system to commercialization).
  - Co-free cathodes are available for Na-ion batteries (the ethics of Co mining are an issue for Li-ion batteries, as well as its cost).
  - Na-ion anodes do not require Cu current collectors, can use Al. This lowers cost and alleviates concerns about Cu, another strategic metal.
  - Na-ion electrolytic solutions are generally 10-15% more conductive than their Li-ion analogs. Can use less electrolyte salt (a cost savings), and/or design cells with thicker electrodes without compromising the energy/power ratio, another cost-savings.
  - State-of-the-art Na-ion batteries match energy densities of Li-ion batteries with  $\text{LiFePO}_4$  cathodes.
- Need better anodes for Na-ion batteries.
  - Safety concerns with the hard carbon anodes currently used
  - Energy density is dependent on anode material (we have good cathodes)
  - Goal of this project is to investigate the possibility of titanate anodes, another goal is to study electrolytes that can enable these electrodes.

# Milestones-FY2019

Milestone	Type	Date/Status
Hydrothermal synthesis of sodium nonatitanate	Milestone	Q1/completed
Ion xch sodium nonatitanate with Mg	Milestone	Q2/completed
Complete synchrotron XRD and XAS	Milestone	Q3/in progress
Go/no go decision on Mg exchange	Milestone	Q4/ no go, because Mg xch worsened properties

Any proposed future work is subject to change based on funding levels

# Milestones-FY2020



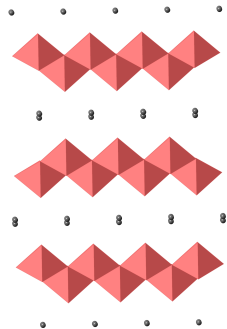
Milestone	Type	Date/Status
SEI studies and electrolytes (XPS, XAS, ATR-FTIR)	Milestone	Q1 2020/planned
Synthesize lepidocrocite titanates	Milestone	Q2 2020/planned
Select best electrolyte solution	Milestone	Q3 2020/planned
Go/no go on sodium nonatitanate	Go/no go	Q4 2020/planned, stop if material doesn't achieve goals.

Any proposed future work is subject to change based on funding levels

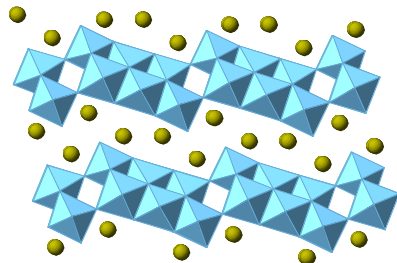


# Approach

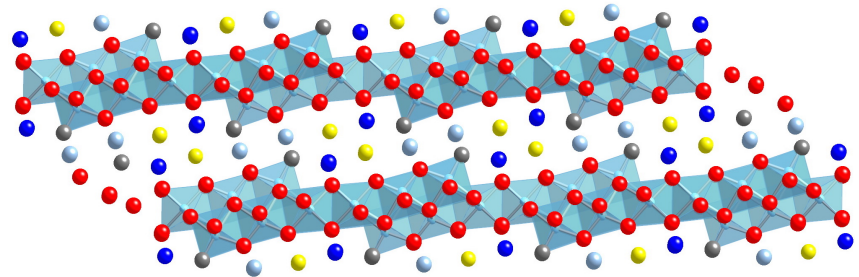
- Candidate titanate anode materials are synthesized and studied.
- Several techniques are used to understand their sodium insertion mechanisms and their interfacial properties. These include *in situ* synchrotron XRD, XAS, XPS and other spectroscopic techniques.
- Some work will be directed towards development of electrolytes and additives (with Dr. Kang Xu of Army Research Lab) and understanding their effect on interfacial chemistry.



Lepidocrocite-type  
Step size=1



$\text{Na}_2\text{Ti}_3\text{O}_7$   
Step size=3



Sodium nonatitanate ( $\text{NaTi}_3\text{O}_6\text{OH}$ )  
Step size=6



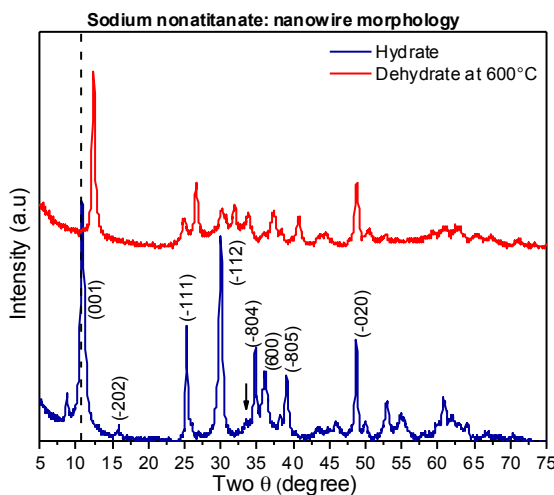
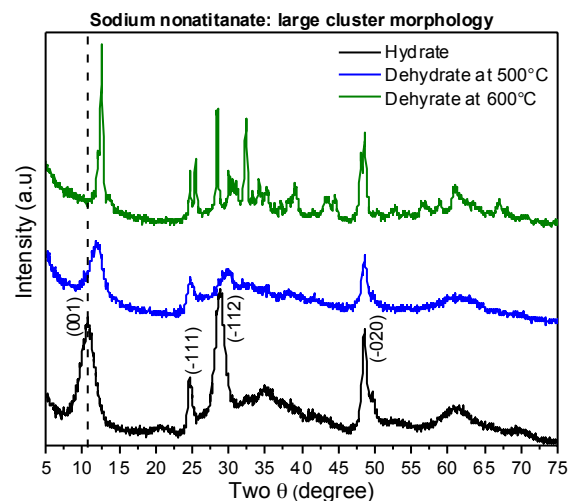
# Background

- There are several corrugated layered Na-Ti-O titanates that reversibly insert Na ions.
  - We have chosen 3 to study initially (see Approach) based on their structural similarities but quite different electrochemical behavior
    - **Lepidocrocite-structured titanates**, step size 1, (variable compositions,  $A_xTi_{2-y}M_yO_4$ ; A=large cation, M=vacancy, Li, Mg, Co, Ni, Fe, Mn, Cu, Zn, etc.)  
Sloping featureless voltage profiles, similar to supercapacitor with  $V_{av} \sim 0.5V$  vs. Na/Na<sup>+</sup>. See M. Shirpour, J. Cabana and M. Doeff, Chem. Mater. 2014, 26 2502.
    - **Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>**, step size=3. Flat voltage profile at  $\sim 0.3V$  vs. Na/Na<sup>+</sup>. Two-phase behavior. (See P. Senguttuvan, G. Rousse, V. Seznec, J.-M. Tarascon and M. R. Palacin, Chem. Mater. 2011, 23 4109.
    - **“sodium nonatitanate” NaTi<sub>3</sub>O<sub>6</sub>(OH)**, step size 6. Sloping featureless voltage profile, similar to supercapacitor, with  $V_{av} \sim 0.3V$  vs. Na/Na<sup>+</sup>. See M. Shirpour, J. Cabana, and M. Doeff, Energy & Environ. Sci. 2013, 6 2538.
- Questions we would like to answer
  - Is the electrochemical mechanism of lepidocrocite structured titanates and sodium nonatitanate different from Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (supercapacitor vs. insertion)?
  - If so, why?
  - Can we exploit supercapacitor behavior to improve energy density?
  - How do the step size differences relate to the electrochemistry? Can we design other materials based on the information we obtain?

# Technical Accomplishments and Progress

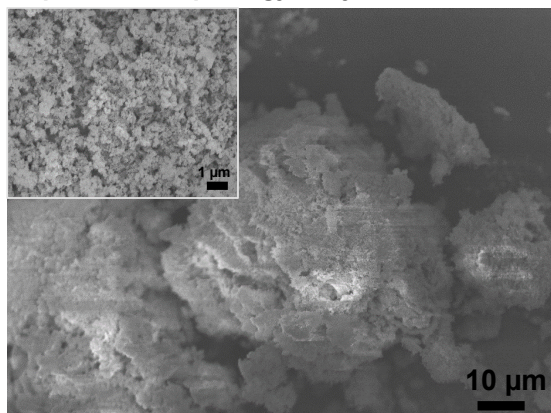


## NaTi<sub>3</sub>O<sub>6</sub>(OH)-sodium nonatitanate

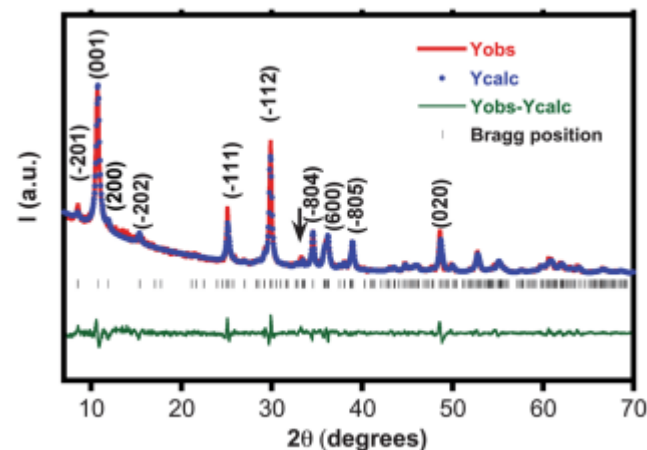
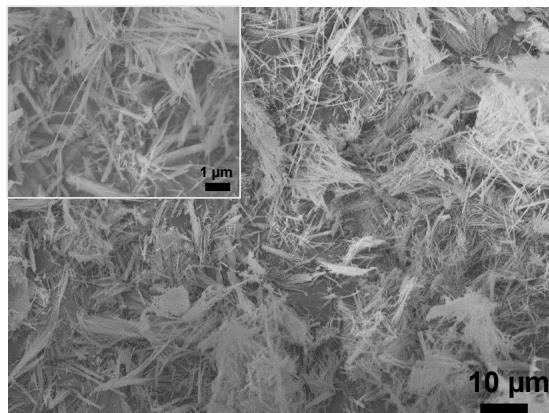


- The hydrate NaTi<sub>3</sub>O<sub>6</sub>(OH)•2H<sub>2</sub>O is synthesized hydrothermally and then dehydrated.
- Morphology and crystallinity is governed by reaction time.
- Clusters (spherical): 20 h at 200°C
- Nanowires: 96 h at 200°C

**Spherical morphology dehydrated at 600°C**



**Nanowire morphology dehydrated at 600°C**

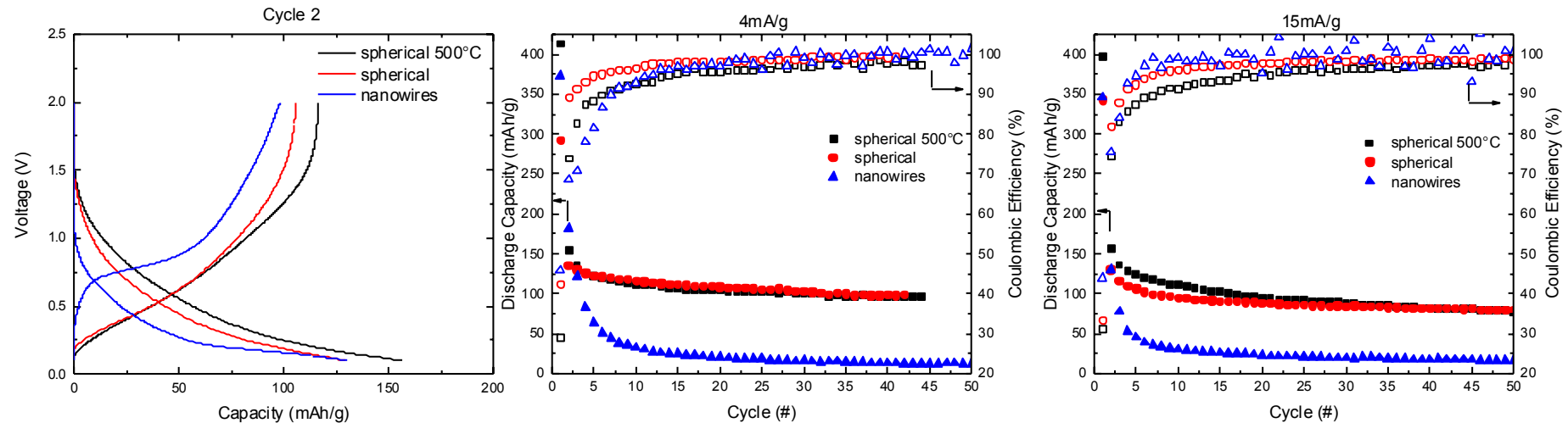






# Technical Accomplishments and Progress

## Electrochemical Performance of sodium nonatitanate samples

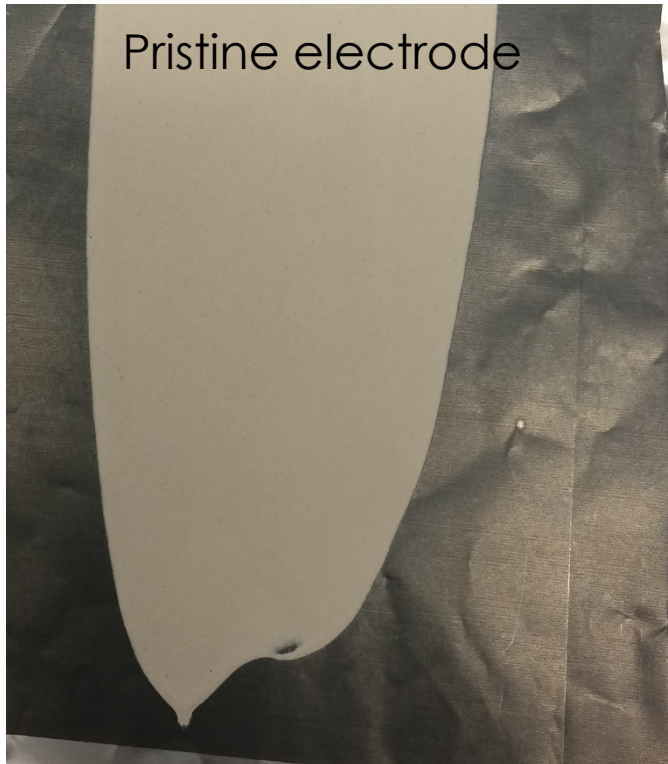


Electrode: AM 70: AB 25: PvDF 5  
Carbon: Acetylene black  
Electrolyte : 1 M NaPF<sub>6</sub> EC:DEC (3:7 wt%)  
Rate: 15 mA/cm<sup>2</sup>  
Mass loading : 2.5-3 mg/cm<sup>2</sup>

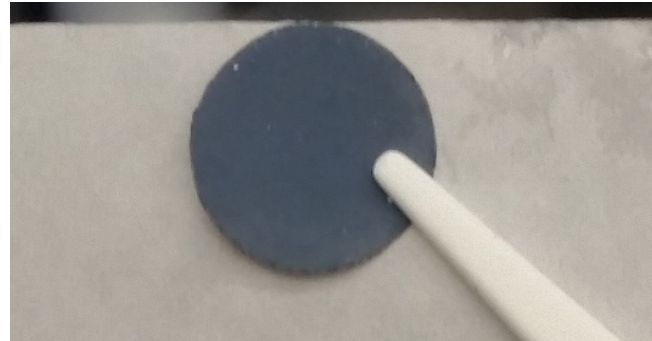
Spherical particles outperform nanowires  
Rate limitations are evident  
Some capacity fading, but cells are not optimized

# Technical Accomplishments and Progress

Sodium nonatitanate-does charge transfer occur?



90 Active material:10 PvDF  
Mass loading: 2mg/cm<sup>2</sup>  
No carbon



Half cell  
current:4 mA/g

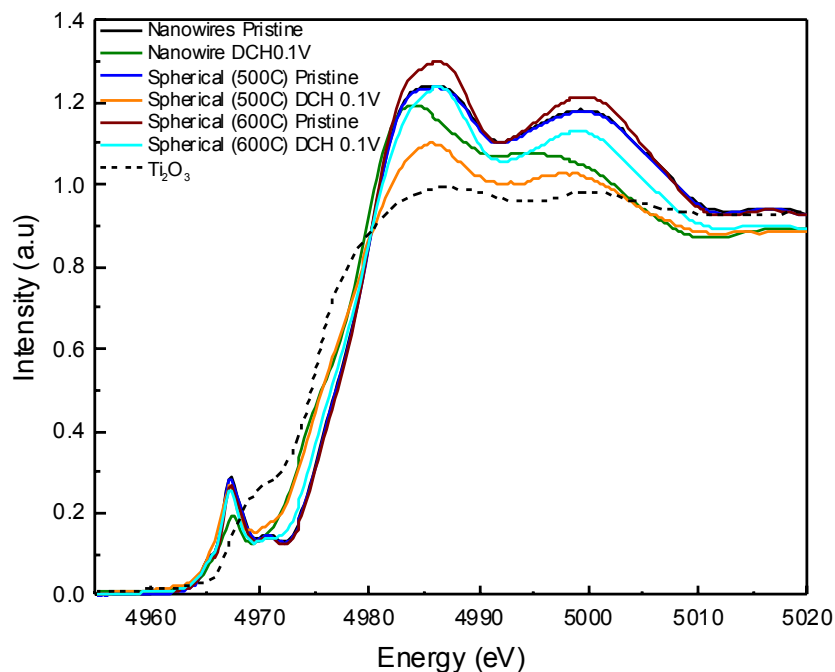
Electrode discharged to 0.1V  
Blue color due to Ti reduction



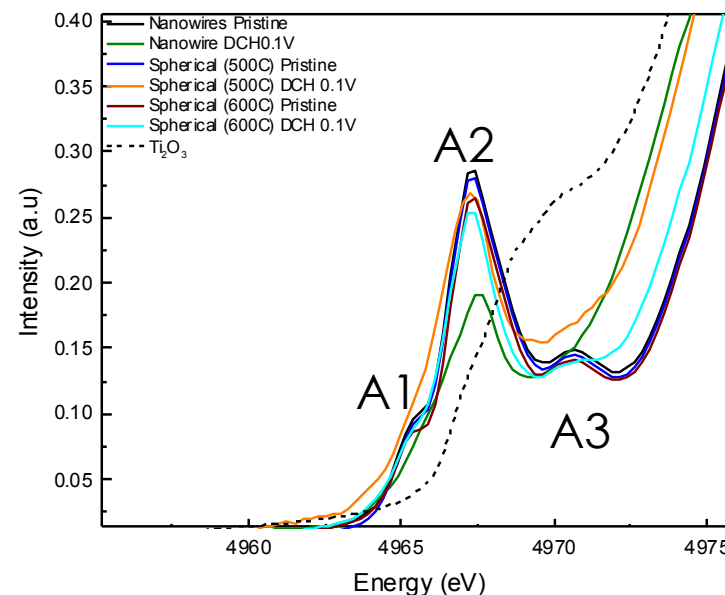
Electrode recharged to 2.0V

# Technical Accomplishments and Progress

## Ex situ Ti K-edge XANES



Changes in XANES for discharged electrodes indicate that some Ti is reduced to the trivalent state.



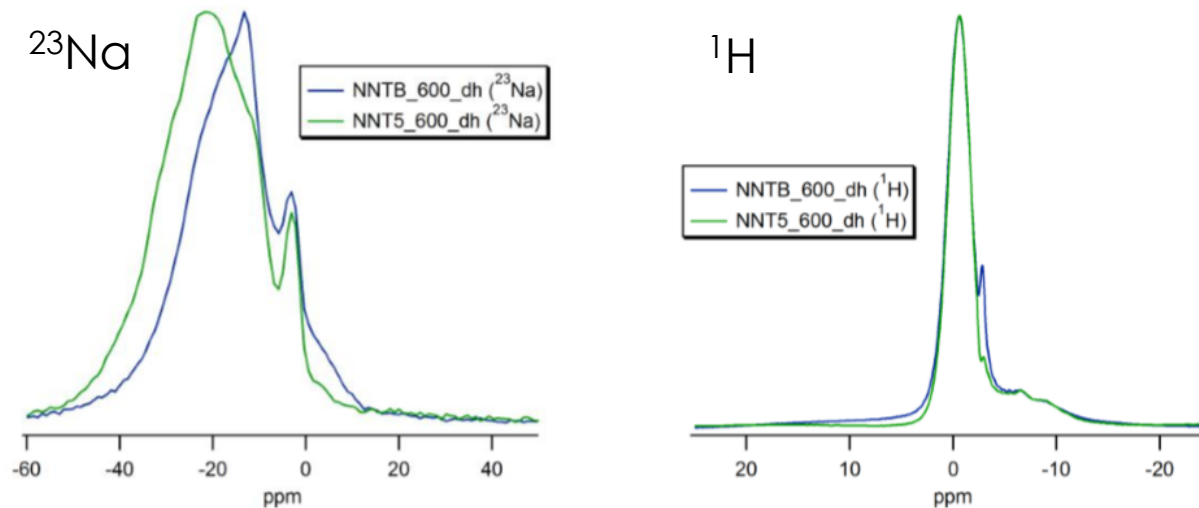
### Pre-edge features

Peaks A1-A3 correspond to transitions of Ti 1s electrons to unoccupied Ti 3d-4s/4p states. Decrease in A1 suggests partial filling of Ti-3d  $t_{2g}$  band (reduction). Nano Lett. 2013, 13, 4721.



# Technical Accomplishments and Progress

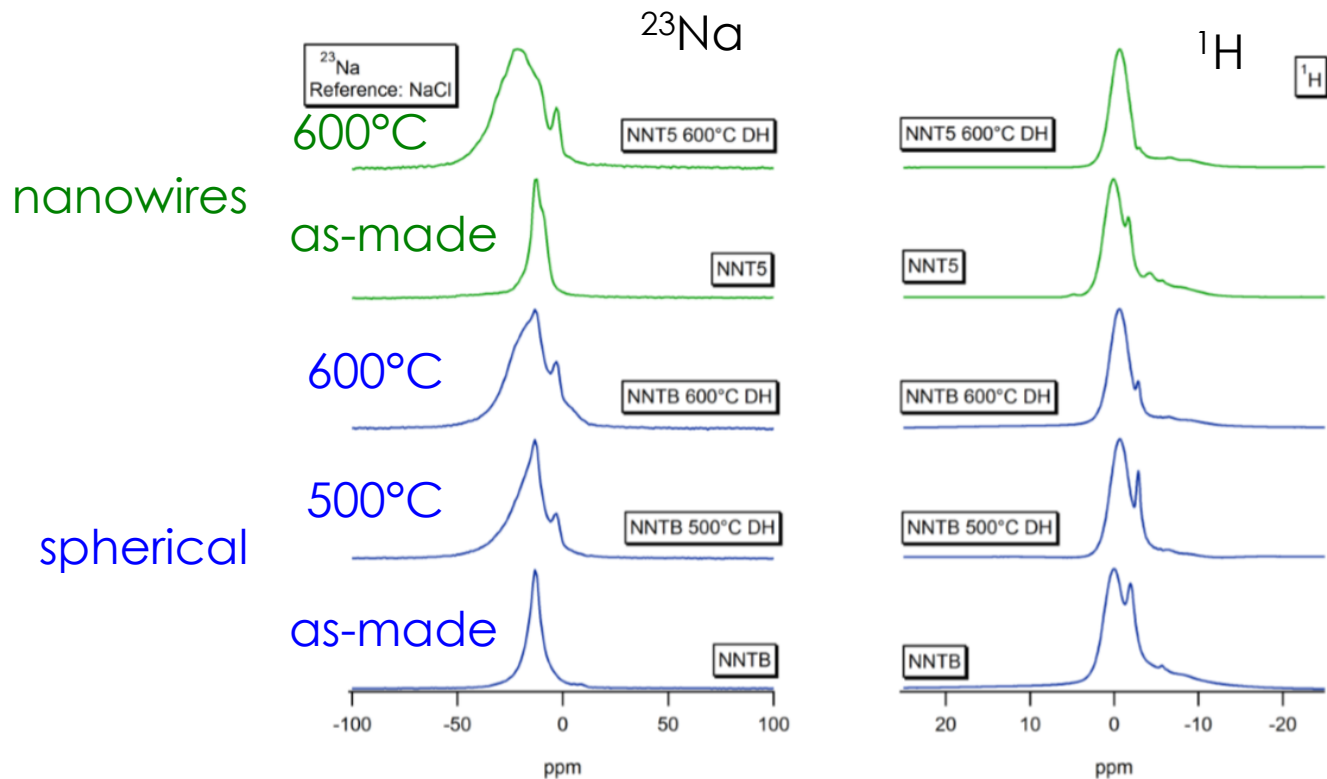
$^1\text{H}$  and  $^{23}\text{Na}$  MAS NMR studies of dehydrated sodium nonatitanate



At least two peaks are seen in  $^{23}\text{Na}$  NMR of dehydrated spherical sodium nonatitanate (blue) and nanowire sodium nonatitanate (green), but these are at different ppm's for the two materials, implying differences in structure/chemistry. Protons are present in both materials, from OH groups in  $\text{NaTi}_3\text{O}_6(\text{OH})$  and/or adventitious water.

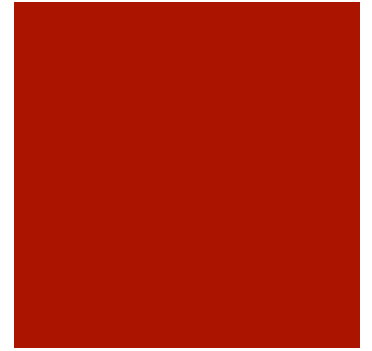
# Technical Accomplishments and Progress

$^1\text{H}$  and  $^{23}\text{Na}$  MAS NMR of as-made and dehydrated sodium nonatitanate



There is one peak in the  $^{23}\text{Na}$  spectra of the as-made materials, corresponding to one equivalent Na position. This splits into at least two peaks upon dehydration, suggesting a structure change. Two types of protons exist for the as-made materials (OH and  $\text{H}_2\text{O}$ ). The peak at negative ppm decreases upon drying, suggesting it belongs to  $\text{H}_2\text{O}$ .

# Summary



- The performance of sodium nonatitanate is highly dependent on morphology. It is not yet known if this is due to kinetic effects, differing contributions from pseudocapacitance, differences in chemistry and/or structure, or a combination of effects. We are designing experiments to understand the origins of the differences.
- Visual observation and XANES experiments indicate that charge transfer does occur (Ti is partially reduced to the trivalent state). It is possible that pseudocapacitance also contributes to capacity, but more work is needed to understand this.
- We were able to move up several milestones having to do with Mg exchange of sodium nonatitanate to increase capacity (see technical backup slides). We made a no-go decision on this approach.

# Collaboration and Coordination with Other Institutions



Collaborator	Role
Kang Xu, Army Research Lab	Electrolyte studies
Daniel Rettenwander and Maria Gombotz, TU Graz	NMR studies
Dennis Nordlund, Apurva Mehta, SSRL	Synchrotron XAS and XRD studies
Isaac Markus, IBM	DFT calculations

# Proposed Future Research



- In the next phase of the work, we will explore different electrolytic solutions, additives and binders with a goal of improving performance. Part of this work will involve studies of SEI formation by synchrotron XPS, XAS, and other techniques (with Kang Xu of Army Research Lab).
- We will make a decision whether or not to continue with sodium nonatitanate. A no-go decision will be made if performance cannot be improved.
- We will move on to lepidocrocite-structured titanates during the next phase.

Any proposed future work is subject to change based on funding levels



# Remaining Challenges and Barriers



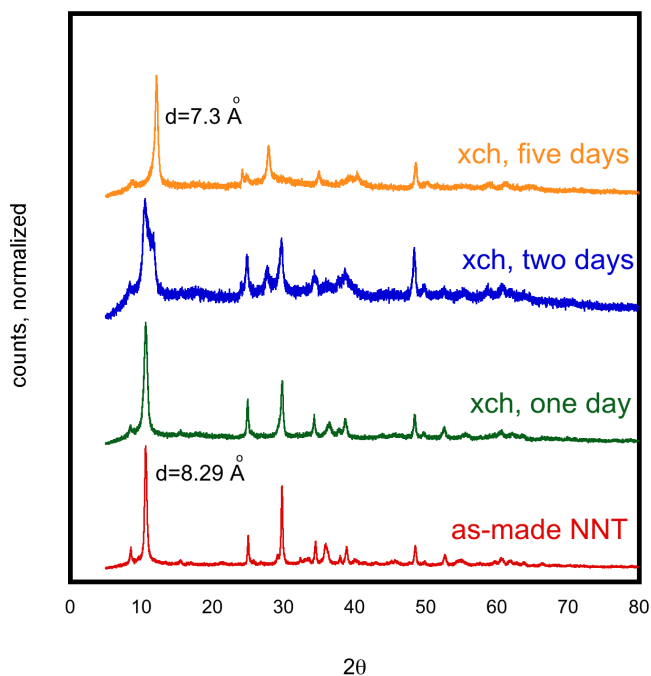
- The sodium nonatitanate structure is very complex. A high number of defects make refinements of patterns very difficult. We will need to employ other methods such as pdf analysis and neutron diffraction to understand the structure.
- We use both in situ and ex situ synchrotron experiments to understand materials. Because of time constraints and limitations in beam time at SSRL, it is not always possible to do experiments in situ.



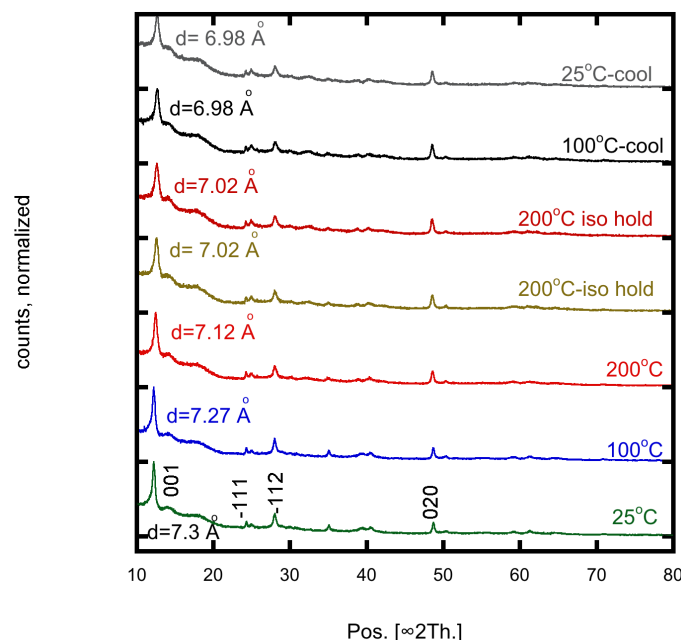
# Technical Backup Slides

# Mg-exchange of sodium nonatitanate

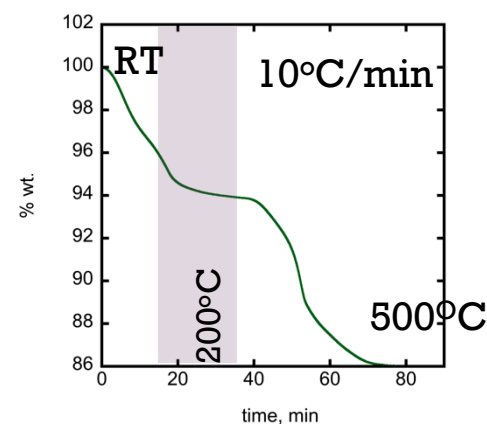
- Premise: by exchanging some or all of the Na in  $\text{NaTi}_3\text{O}_6(\text{OH})$  with Mg, additional sites for intercalation are freed. (1 Mg replaces 2Na)
- 190 mAh/g for unexchanged material increases to 249 mAh/g for fully exchanged material.



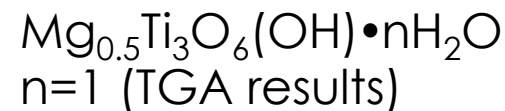
Full exchange after 5 days



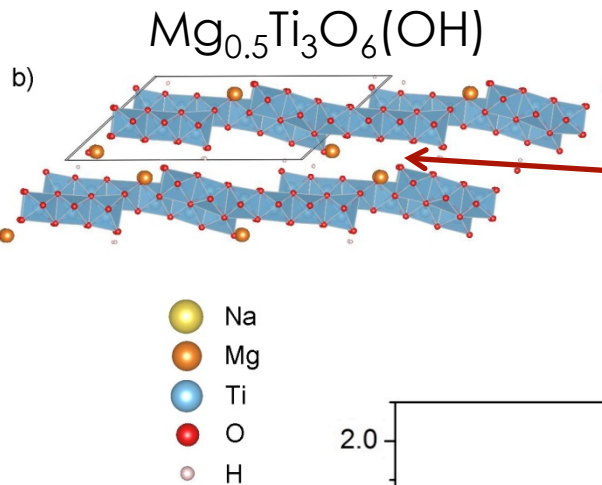
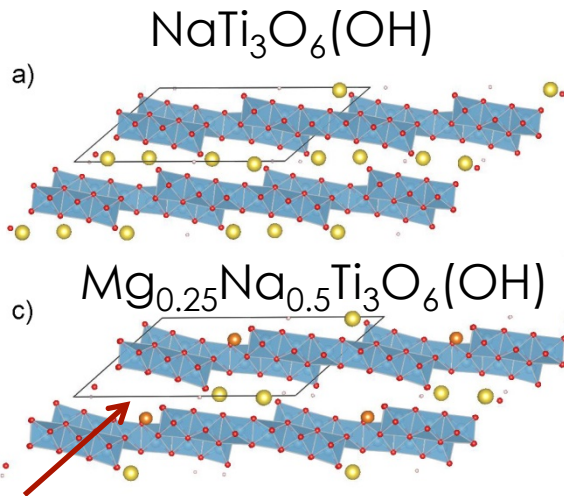
Dehydration at 200°C



TGA data

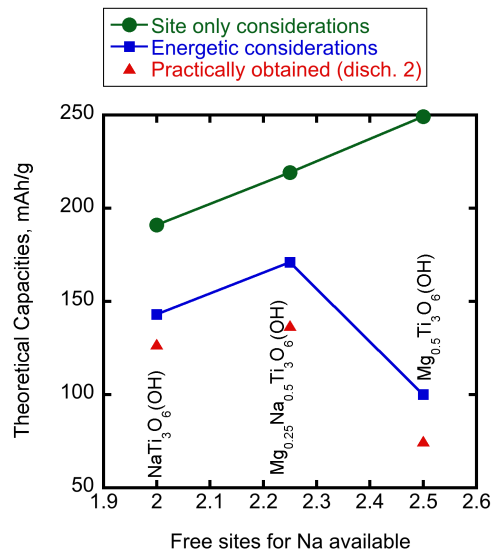


# DFT calculations



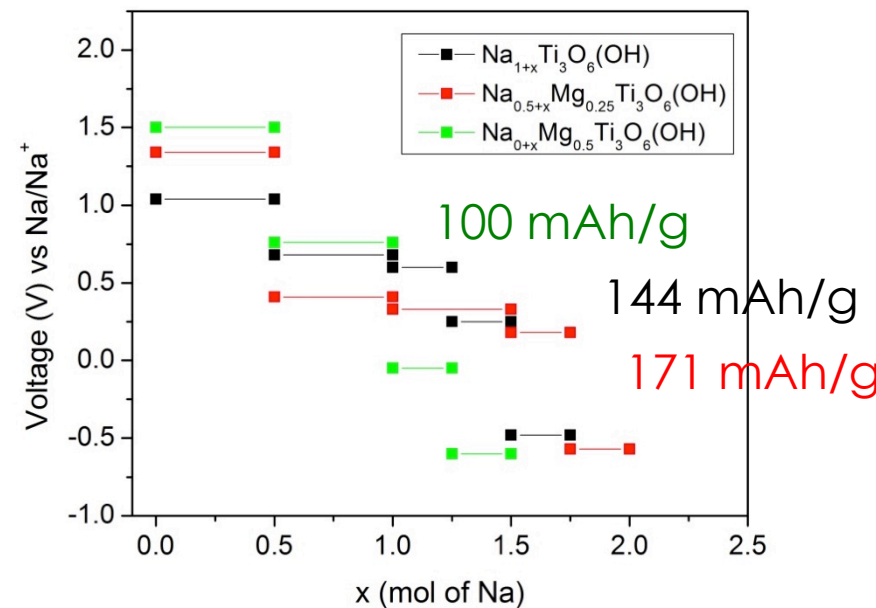
Mg pulled into corrugations block diffusion

More homogeneous ion distributions



Experimental results agree with DFT calculations

I. Markus



Partial exchange is predicted to give better results than full exchange